

# Counter current extraction of phosphoric acid: food grade acid production

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Received 2005-10-19

## Abstract

Extraction, scrubbing and stripping of phosphoric acid from the Syrian wet-phosphoric acid was carried out using Micro-pilot plant of mixer-settler type of 8 l/h capacity. Tributyl phosphate (TBP)/di-isopropyl ether (DIPE) in kerosene was used as extractant. Extraction and stripping equilibrium curves were evaluated. The number of extraction and stripping stages to achieve the convenient and feasible yield was determined. Detailed flow sheet was suggested for the proposed continuous process. Data obtained include useful information for the design of phosphoric acid extraction plant. The produced phosphoric acid was characterized using different analytical techniques.

## Keywords

vanadium · extraction · DEHPA/DIPE

## Acknowledgement

The authors would like to express their thanks to the General Director of the Syrian Atomic Energy Commission Prof. I. Othman for his encouragement to carry out this work, and to the Head of the Chemistry Department. The authors would like to extend their thanks to Ms. S. Alike for her valuable help to carry out this work.

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## 1 Introduction

Solvent extraction of phosphoric acid is usually carried out with organic solvents, such as butyl and isoamyl alcohol and tributyl phosphate (TBP). (Oparin et al [1]) used isopropyl alcohol for phosphoric acid extraction. The aqueous feed was mixed with strong NaOH and ammonia before extraction. The purified  $H_3PO_4$  containing 53%  $P_2O_5$ , 0.02 %  $F^-$  and traces of Fe, Al, Mg, Ca and sulfate. (Ruiz et al [2]) published physical and chemical information about the system  $H_3PO_4$ -water-isomyl alcohol. Distribution coefficient of cationic impurities and  $H_3PO_4$  are given. (Ruiz et al [3]), also investigated the prosperities of dibutyl ether as solvent for purification of  $H_3PO_4$ . The  $H_3PO_4$  extraction capacity of dibutyl ether is similar to propyl ether but, lower than isomyl alcohol. The purification behavior for metallic impurities and sulfate is good, however, not very suitable for  $F^-$  purification. (Farbwerk Hoechst AG [4]) claimed a patent, in which a procedure for phosphoric acid extraction with water-immiscible organic solvents is discussed. A process for simultaneous removal of cationic and anionic impurities from wet phosphoric acid by extracting  $H_3PO_4$  with n- and isobutyl alcohol after the addition of sulfuric acid to the aqueous feed was presented by (Toyo Soda manufacturing Co. Ltd. Japan [5]). (Davister et al [6]) used TBP and di-isopropyl ether (DIPE) in kerosene for phosphoric acid extraction from wet  $H_3PO_4$ . It was claimed that two thirds of the acid could be extracted in four counter current stages at room temperature. In our previous work [7], phosphoric acid was extracted using a mixture of TBP and kerosene with the volume ratio of 80:20, where the total extraction yield reached about 50%. Recently we have improved the yield of phosphoric acid extraction from the barren raffinate acid (36-wt%  $H_3PO_4$ ) to about 80% using a synergistic solvent mixture TBP/DIPE in kerosene on bench scale level [8]. In this present work, a proposed continuous process for phosphoric acid extraction is presented. A micro pilot plant of 8 l/h capacity, was used for phosphoric acid counter current extraction from the  $H_3PO_4$  (raffinate) produced at uranium extraction unit from the Syrian crude phosphoric acid. Determination of the number of stages needed for extraction, scrubbing and stripping to produce food grade phosphoric acid was carried out, too.

Furthermore, the produced acid was concentrated by evaporation and characterized.

## 2 Experimental

### 2.1 Reagents

Extraction was carried out using the raffinate phosphoric acid 36 wt% produced at the Syrian uranium recovery unit. Acid used was pretreated to eliminate solid materials by filtration using Barite column, and organic materials using active carbon column. The treated acid contained 5 mg/l and < 5mg/l of solid and organic materials, respectively and its optical Density=0.01 at 405 nm. Table below shows the main composition of the treated acid.

Tributyl phosphate (TBP) 99% and di-isopropyl ether (DIPE) 99% were supplied by Merck. Kerosene with a flash point of 76°C used as diluent was supplied by Pemco Chemical AB and contained less than 0.5% aromatics.

### 2.2 Apparatus and procedures

Micro pilot plant of 8 l/h capacity provided with controlled agitators has been used. Mixers dimensions are: L: 12 cm, W: 12 cm and H: 15 cm. Settlers dimensions are: L: 18 cm, W: 12 cm and H: 18 cm. Raffinate phosphoric acid produced at the Syrian uranium extraction unit salted with 4 v/v%  $\text{H}_2\text{SO}_4$  and 4 g/l NaCl (in order to improve the extraction yield [8]) was used to extract phosphoric acid by the synergetic organic phase mixture of 1/9 ratio of DIPE/TBP in 20% kerosene. Flow rates of acid and organic were 2 and 6 l/h, respectively. Internal recycle of the acid phase from settler to mixer is provided to maintain mixer ratio of org/aqu to 1/1.5 to achieve continuous flow of aqueous phase and to improve the phase separation. Loaded organic phase scrubbing was carried out using laboratory grade phosphoric acid (36 wt%) under the following conditions: temperature 25°C, aqueous flow rate 0.5 l/h, organic flow rate 6 l/h and three scrubbing stages, the scrubbing solution was recycled to the feed acid in the extraction part. Organic phase stripping was carried out using diionized water under the following conditions: temperature 25°C, organic phase flow rate 6 l/h, aqueous flow rate 2 l/h and four stripping stages, continuous flow of aqueous phase was achieved by maintaining the mixers phase ratio of org/aqu to 1/1.5. Flow-rate of aqueous and organic phases was calibrated to maintain their retention time in mixers of more than 5 minutes. Fig. 1 represents the schematic process flow sheet for all steps of the proposed process.

The diluted phosphoric acid produced was concentrated by evaporation and characterized by AAS, ICP and XRF.  $\text{H}_3\text{PO}_4$  concentration was determined by titration with 1.0 M NaOH using a potentiograph E536 from Metrohm.

## 3 Results and discussion

### 3.1 Counter-Current phosphoric acid extraction

Barren raffinate Acid produced at uranium extraction unit was used for phosphoric acid counter-current extraction with the mi-

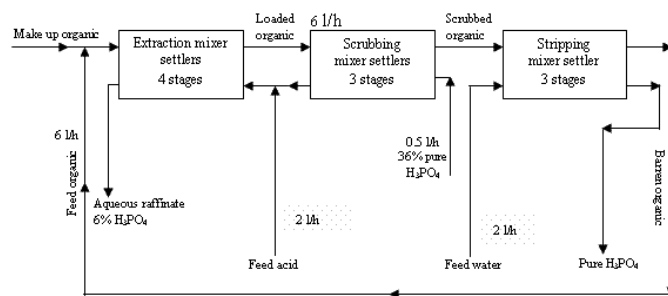


Fig. 1. Schematic flow sheet for the proposed process.

cro pilot-plant. 2 l/h of the salted out phosphoric acid pumped in to the Micro pilot plant (feed acid), 6 l/h of the organic phase (DIPE/TBP in kerosene) pumped also (feed organic). Phase ratio in the mixer was maintained by recycling the acid from the settler to the mixer (aqueous is continuous) in order to improve the phase separation. Four counter current extraction stages were used. Aqueous and organic samples from the settlers of each stage were taken during the operation of the micro pilot after reaching steady state. Phosphoric acid concentration of samples was determined and results were used to draw the operating line as illustrated in Fig. 2. Bench scale extraction of  $\text{H}_3\text{PO}_4$  was carried out using different phase ratios of org/aqu under the following conditions: Temperature 25 °C, mixing and settling time 10 min. Acid concentrations in both phases were determined. Results were used to draw the extraction equilibrium curve illustrated also in Fig. 2. According to the method of McCabe & Thiele, it was found that five counter current extraction stages are needed to achieve more than 90% extraction yield of  $\text{H}_3\text{PO}_4$ .

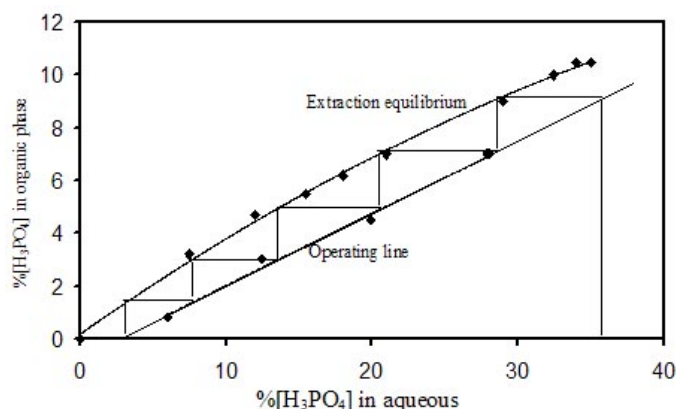


Fig. 2. Number of extraction stages by the McCabe method

### 3.2 Organic phase scrubbing

The obtained loaded organic from the extraction stages, was analyzed to determine impurities concentration. Table below shows the concentration of the main impurities found in the loaded organic.

Elimination of the impurities was carried out in three scrubbing stages operated co-currently using laboratory grade  $\text{H}_3\text{PO}_4$  (36 wt%) as a scrubbing agent under the following conditions: Temperature 25 °C, organic flow rate 6 l/h, aqueous flow rate

0.5 l/h, Org:Aqu ratio in mixer is 1:1.5 (aqueous is continuous). Determination of the outlet organic phase from the scrubbing stages showed that more than 95% of the main impurities have been eliminated.

### 3.3 Phosphoric acid stripping

The loaded and scrubbed organic phase was stripped with di-ionized water in four stages under the same conditions of the scrubbing process. Organic and aqueous samples from each of the four settlers were taken and  $\text{H}_3\text{PO}_4$  concentration was determined. Results were used to draw the operating line. Bench scale stripping of  $\text{H}_3\text{PO}_4$  from the loaded organic phase was carried out using different phase ratios of org/aqu under the following conditions: Temperature  $25^\circ\text{C}$ , mixing and settling time 10 min. Acid concentrations in both phases were determined. Results were used to draw the stripping equilibrium curve. Stripping equilibrium curve and the corresponding operating line are represented in Fig. 3 which shows that four stripping stages are needed to achieve a stripping yield of more than 95%.

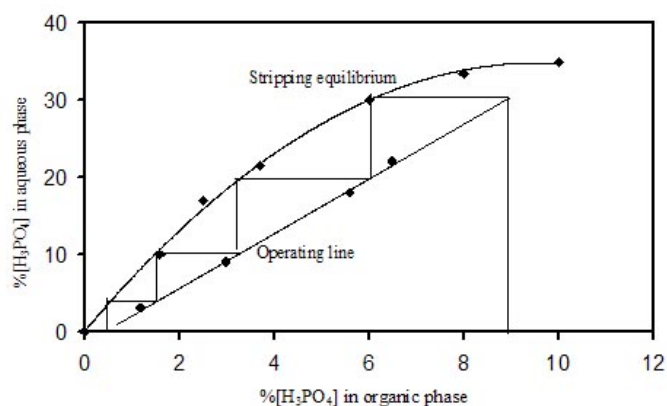


Fig. 3. Number of stripping stages by the McCabe method

### 3.4 Characterization of the produced Phosphoric acid

The outlet stripping liquor contains about 26 wt% phosphoric acid, it was concentrated by evaporation. AAS, ICP and XRF analysis techniques were used for the final product acid characterization. Results are represented in table below which, shows that the purification behavior for metallic impurities is good, however, not very suitable for  $\text{F}^-$  and sulfate. Which, could be eliminated in advance during the acid evaporation (Post-treatment) by steam stripping technique, using specific design evaporation column in the industrial units. The amounts of both  $\text{F}^-$  and S were minimized to  $< 50$  ppm at the Syrian Pilot-plant using this process.

## 4 Conclusion

The obtained results showed that:

Using the organic phase of TBP/DIPE in kerosene, enabled us to achieve 80% and more than 90% extraction yield of  $\text{H}_3\text{PO}_4$  from the Syrian wet phosphoric acid (Raffinate) in four and five counter current extraction stages, respectively. Three

Tab. 1. Composition of the feed acid, loaded organic and the pure  $\text{H}_3\text{PO}_4$  produced.

Elements Con. (ppm)	Feed acid (Raffinate)	Loaded organic	Pure $\text{H}_3\text{PO}_4$ produced
S	7350	400	250
$\text{Cl}^-$	592	8	-
Ca	613	33	12
Ti	26	18	-
V	65	4	-
Cr	101	1.5	-
Fe	1850	12	8
Ni	13.1	-	-
Cu	6.3	1.1	$< 1$
As	0.1	-	-
U	1.5	-	-
$\text{F}^-$	2.2 %	0.8 %	1 %
Zn	204	3.5	-

counter current scrubbing stages and four stripping counter current stages, were sufficient to produce pure and food grade phosphoric acid. Sulfur and fluoride contents can be eliminated by steam stripping technique during the acid concentration.

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